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CAPILLARY DECOMPOSITION OF EXPLOSIVES AND ANALYSIS BY EITHER VAPOR-PHASE CHROMATOGRAPHY OR THE COMBINATION OF THIN-LAYER CHROMATOGRAPHY AND VISIBLE SPECTROMETRY

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SUMMARY

A method for the capillary decomposition of explosives and subsequent analysis by either vapor-phase chromatography or the combination of thin-layer chromatography and visible spectrometry is described. The utility of the method is illustrated with the isothermal decomposition of liquid 2,4,6-trinitrotoluene at 260°.

INTRODUCTION

We recently reported a method for measuring the extent of the thermal decomposition of explosive compounds based on the analysis of residual explosive after a specified heating time by a combination of thin-layer chromatography (TLC) and visible spectrometry[1]. The method consisted of accurately weighing 0.1 to 0.2 g of the explosive into a 10-ml pyrex glass tube, which was then evacuated and sealed prior to heating. Analysis of residual explosive was accomplished by dissolving or extracting the contents of the opened tube into a known volume of solvent and spotting aliquots of this solution on TLC plates. After development, zones containing the explosive were extracted and analyzed spectrophotometrically as their ethylenediamine complexes in dimethyl sulfoxide solution[2]. More recently, this work has been extended to include analysis of nitro compounds by vapor-phase chromatography (VPC) with the extremely sensitive nickel-63 electron capture detector[3].

The decomposition of an explosive in a sealed capillary and its subsequent work-up in the simple apparatus described offers a new technique which not only uses much less explosive and hence is safer, but in addition, employs fewer steps and is more rapid as well as potentially more accurate. Furthermore, the capillary technique offers the opportunity to observe interactions of various substances with an explosive on a very small scale. We wish now to describe this technique and the apparatus used. As an illustrative example, the high-temperature isothermal decomposition of 2,4,6-trinitrotoluene (α-TNT) as a function of time is given.

EXPERIMENTAL

Apparatus for breaking and extracting contents of capillaries

The apparatus as shown in Fig. 1 consisted of a No. 4 standard tapered Pyrex

stop-cock located between two segments of 10 mm O.D. Pyrex tubing. The bottom segment was approximately 45 mm long and sealed at the end. The top segment was also approximately 45 mm long and fitted with a standard tapered 10/30 glass stopper. In addition, the top segment was calibrated in millimeters for a distance of 25 mm above the stop-cock. The overall length of both segments through the stop-cock was 108 mm. The stop-cock was lightly lubricated with Dow Corning high-vacuum grease and held tightly in place by a spring clip. In practice it was found best to calibrate the apparatus by pipetting exactly 2 ml of solvent into the dry apparatus and noting the volume on the calibrated scale portion. Subsequent volumes were then adjusted to this mark by simple addition of solvent.

Capillary tubes

The capillary tubes used were Kimas-51 brand with 1.6 × 1.8 × 90 mm dimensions. The tubes were used as received and were sealed after sample introduction with a CRC miniature "flamidget" butane/oxygen welding torch. The capillaries

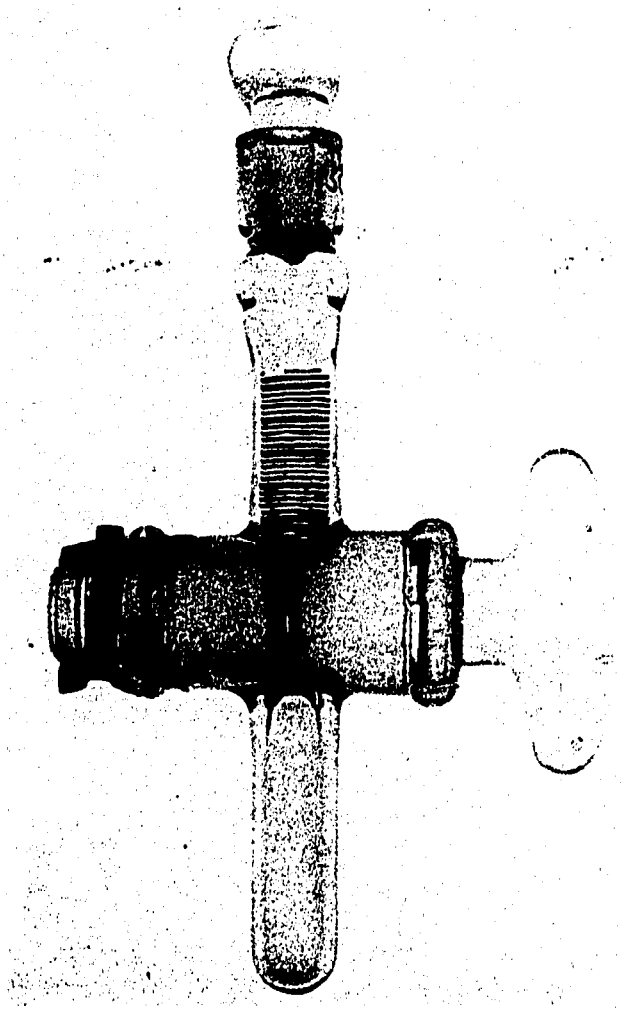

Fig. 1. Apparatus for breaking sealed capillaries under solvent.

could also be evacuated prior to sealing by means of an 1/8 in. ultra-torr to 1/4 in. stainless-steel adapter connected to a vacuum pump.

Vapor-phase chromatography of α-TNT

The following conditions were found to be optimum for the quantitative analysis of α-TNT with 1,2-dinitrobenzene as internal standard (IS): A 4 ft. × 1/4 in. glass column packed with 2.53 % Apiezon M on Diatoport-S 60/80 mesh; carrier gas, Ar–CH_4 (95:5); flow rate, 67 ml/min; purge rate, 108 ml/min; column temperature, 165°; injection port temperature, 195°; Ni-63 detector temperature, 280°; pulse interval, 150 μsec; attenuation, × 40. With these conditions, the retention time for α-TNT was found to be 0.71 min, and 1.67 min for 1,2-dinitrobenzene, both measured from the solvent–pressure peak. Typical responses for a 1-μl injection of a mixture of 1.78×10^{-9} g/μl α-TNT and 1.26×10^{-10} g/μl 1,2-dinitrobenzene in benzene (MCB, specially purified for work with electron capture detectors) were found to be 152 and 135 mm for the peak heights, respectively.

Visible spectrometry (Cary 16 spectrophotometer)

Visible spectrometry yielded the following extinction coefficients (ε): (1) 1,4-dipicrylbenzene, $\lambda_{max.} = 458$ nm: $\varepsilon = 63\,500$ in ethylenediamine (EDA)–dimethyl sulfoxide (DMSO) (0.1:9.9); (2) α-TNT, $\lambda_{max.} = 464$ nm: $\varepsilon = 23\,200$ in EDA–DMSO (8:2) and α-TNT, $\lambda_{max.} = 460.7$ nm: $\varepsilon = 21\,000$ in EDA–CH_3OH (5:5); (3) 1,3-diamino-2,4,6-trinitrobenzene, $\lambda_{max.} = 331.5$ nm: $\varepsilon = 18\,750$ in DMSO.

Solvents for TLC development

Benzene–hexane (1:1) was used for α-TNT (R_F 0.45), while benzene–ethyl acetate–hexane–pentane (45:5:5:5) was used for 1,4-dipicrylbenzene (R_F 0.63) and 1,3-diamino-2,4,6-trinitrobenzene (R_F 0.46).

Preparation of TLC plates

Thirty grams of Silica Gel HF_{254} (Brinkman) were vigorously slurried for 2 min in 65 ml of distilled water in a 500-ml erlenmeyer flask and spread on to eleven to twelve TLC plates with a Camag applicator. The plates were air dried at ambient temperatures for 3 to 4 h, then dried at 110° in an oven for 1.5 h. The dried plates were stored at room temperature in a closed container.

RESULTS AND DISCUSSION

Capillary method of analysis

To test the feasibility of the capillary method for the decomposition of explosives, several explosives were weighed into capillaries; the capillaries were evacuated, sealed and finally crushed under solvent in the apparatus shown in Fig. 1. Care was taken in loading and weighing capillaries to avoid any contamination due to handling. Nylon gloves were preferred when handling capillaries. Capillaries could also be weighed accurately by carefully wiping the outside of the tubes with a clean tissue after loading. Five repeated weighings of a single capillary gave on the average 0.184639 ± 0.000006 g, which represents a potential error of only about 0.1 % for a 6-mg sample weighed into the capillary.

The loaded capillary was placed in the apparatus with 2 ml of solvent (acetone for α-TNT and 1,4-dipicrylbenzene; DMSO for 1,3-diamino-2,4,6-trinitrobenzene). The capillary was then thoroughly crushed by turning the stop-cock back and forth, and the contents were extracted by vigorously shaking the crushed pieces in the stoppered apparatus. Analyses of these solutions were made either spectrophotometrically or by VPC by taking aliquots of the 2-ml solution and diluting to 10 ml in the appropriate solvent. The recoveries based on these analysis are shown in Table I.

As seen from the data in Table I, the average percentage recovery based either on visible spectrometry or VPC is 99.8 ± 1.5 %. Calculations of the weight, g, in grams of material in the capillary by spectrophotometric analysis were made from the following expression:

$$g = (\text{O.D.})/\varepsilon \times (\text{M.W.})/V \times 0.02,$$

where O.D., ε, and M.W. are the experimental optical density, extinction coefficient, and molecular weight of the compound being determined, and V is the aliquot volume in milliliters of the solution (total volume, 2 ml) diluted to a final volume of 10 ml. Calculations of the weight, g, in grams of the α-TNT in capillaries by VPC analysis were made from the following expression:

$$g = nh_x/h_{std} \times C_{std} \times 2/V,$$

where h_{std} and C_{std} represent the chromatographic peak height and the concentration of standard (std) in grams per 10 ml, respectively, and V is the aliquot volume in milliliters of the acetone solution (total volume, 2 ml) diluted to 10 ml. nh_x is the normalized sample (x) peak heights for the same amount of internal standard (IS) in both sample and standard solutions, and is expressed by the expression:

$$nh_x = \mu l_{IS}(x)/\mu l_{IS}(std) \times h_{IS}(std)/h_{IS}(x) \times h_x.$$

TABLE I

RECOVERIES OF KNOWN QUANTITIES OF EXPLOSIVES IN SEALED CAPILLARIES BASED ON SPECTROPHOTOMETRIC AND VPC ANALYSES

Compound	*Actual weight in capillary (mg)*[a]	*Weight found*[b]	*Method of analysis*	*% Recovery*
1,4-Dipicrylbenzene	6.22	6.24	Spectrophotometry[c]	100.3
1,3-Diamino-2,4,6-trinitrobenzene	3.54	3.48	Spectrophotometry[d]	98.3
α-TNT	6.18	6.06[e]	VPC	98.1
	4.30	4.40[f]	VPC	102.3

[a] Weighed into capillary by difference on a Mettler microgram-atic balance.

[b] After crushing and extracting contents of capillary into 2 ml solvent in apparatus.

[c] 15 μl diluted to 10 ml in DMSO–EDA, 9.9:0.1; O.D. = 0.5930 at 458 nm.

[d] 25 μl diluted to 10 ml in DMSO; O.D. = 0.3356 at 331.5 nm.

[e] 6 μl diluted to 10 ml in benzene and 35 μl of 3.61×10^{-8} g/μl 1,2-dinitrobenzene added as IS. 1 μl of this solution gave the following IS/α-TNT peak heights: 135.9/155.6 (sample), and 135.0/152.0 (standard; see EXPERIMENTAL for standard concentrations).

[f] 8 μl diluted and treated as described in the above footnote[e]. 1 μl of diluted solution gave the following IS/α-TNT peak heights: 127.4/133.0 (sample), and 121.0/133.0 (standard).

Thermal decomposition of α-TNT in capillaries

The thermal decomposition of liquid α-TNT at 260° was measured as a function of time by the capillary method described. Capillaries were loaded with 4 to 6 mg of α-TNT, evacuated, sealed and placed in an open 10-ml test tube in a small heating block which could be maintained within ±0.3° of 260°. By actual measurement, the time for capillary heat-up to 260° was 5 min. Analyses of the residual α-TNT at a specific time were accomplished by both VPC and the combination of TLC and visible spectrometry. In the latter case, 25-μl aliquots of the extracted residue in 2 ml of acetone solution were developed on TLC plates, and the separated α-TNT zones were made visible under 2537 Å UV light, scraped off, extracted and analyzed spectrophotometrically as previously described[1]. These results are shown in Table II.

The agreement between the two methods is excellent and indicates that the α-TNT decomposition by-products do not interfere with the VPC analysis of α-TNT. At least five decomposition products in addition to residual α-TNT were observed on TLC plates under UV light. One product, the 4,6-dinitroanthranil, corresponds to the product previously isolated by DACONS *et al.* of this laboratory[4]. The overall accuracy by the capillary method of analysis of residual α-TNT either by VPC chromatography or by the combination of TLC and visible spectrometry is between 1 and 2 %.

TABLE II

THERMAL DECOMPOSITION OF LIQUID α-TNT AT 260° IN SEALED CAPILLARIES

Time (min)	*Initial α-TNT in capillary (mg)*	*Residual α-TNT in capillary (mg)*		*% Decomposition (both methods)*
		VPC	*Spectrophotometry*	
10	4.89	4.70; 4.59	4.51[a]	6.3 ± 1.6
15	4.06	4.37; 4.52	4.44[a]	10.4 ± 1.6
20	5.17	4.33	4.23[a]	17.4 ± 1.6
30	5.34	3.62	3.62[b]	32.4 ± 0
35	6.36	4.18; 4.00	4.11[b]	35.5 ± 1.6
40	5.01	0.648	0.646[b]	87.1 ± 0.2

[a] Analyzed in EDA–DMSO (8:2).

[b] Analyzed in EDA–CH_3OH (5:5). Methanol was chosen for extraction and subsequent analysis since extraction of α-TNT from a new lot of Silica Gel HF_{254} TLC plates led to a purple coloration before addition of EDA. Subsequent addition of EDA and analysis led to low values for α-TNT.

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